

FUTURE OF ETHYLENEDIAMINE IN GALVANIC INDUSTRY

N. V. Osetrova

Ethylenediamine electrolytes are of interest because of good solubility of complex salts of a $[\text{MeEn}_m^*]\text{X}_n$ composition, high strength of complexes, stability thereof in aqueous solution, and absence of toxic properties.

We have conducted a series of investigations [1-5] of electrochemical characteristics and properties of electrolytic deposits during electrodeposition from aqueous solutions of some ethylenediamine complexes, and the results obtained suggested the appropriateness of using ethylenediamine for electrodeposition of some metals. Because the research was focused on practical implementation of electrodeposition, the metals were selected that directly form ethylenediamine complexes in interaction of aqueous solutions of simple salts thereof with ethylenediamine. Thus, copper, zinc, cadmium, nickel, and cobalt were selected. Iron, silver and chromium also form complexes with ethylenediamine, but the electrolytes of these metals are more difficult to prepare.

In all five investigations, the types of anions of simple salts that ensure sufficiently good solubility in electrodeposition processes (more than 1 N) were initially determined because quantitative data on solubility of complex amines with various anions are not available. Chlorides of all the metals were found to meet the requirement relating to sufficient solubility, whereas sulfuric acid and fluoroboric acid amines of zinc, cadmium, nickel, and cobalt have a substantially lower solubility. Copper salts have high solubility (3-4 N) for all anions.

Basic characteristics of electrodeposition process were obtained for all the metals in 1 N solutions with different excess amounts of ethylenediamine and different anions that have sufficient solubility.

Electrodeposition of copper from ethylenediamine electrolytes proceeds with a high current yield (90-98%), this yield increasing with the current density.

The allowed current density in copper ethylenediamine electrolytes at which dendrite-free smooth deposits can be obtained is 2-4 A/dm². Contact displacement of copper by iron from

* En – ethylenediamine (NH₂-CH₂-CH₂-NH₂)

ethylenediamine electrolytes is not observed, thereby suggesting the possibility of direct copper deposition on iron. The deposit appearance can vary from matte to mirror glossy, depending on the process conditions and electrolyte composition. Glossy deposits are formed because of passivation of electrode surface, and the passivation is due to surface active properties of ethylenediamine, which can be adsorbed on the cathode surface, thereby forming a passive film [4]. This is apparently why the increase in concentration of free ethylenediamine in electrolyte of any composition increases the degree of gloss. The degree of gloss varies as the current density changes because the adsorption effect is controlled by electrostatic interaction of particles. As the current density and, therefore, cathode potential changes, the interaction of particles can be weakened or enhanced depending on the zero charge potential.

All copper coatings that were obtained from chloride, sulfate, and fluoroborate electrolytes containing excess ethylenediamine and having $\text{pH} > 11$ were glossy at the usual values of current density ($1\text{--}4 \text{ A/dm}^2$). Where the pH value of solution was decreased (an acid was introduced), matte deposits were obtained on the cathode, provided that the ethylenediamine concentration was the same. This phenomenon was explained by the change in the electric nature of particles, that is, by the transition of molecular ethylenediamine into cations EnH^+ and EnH_2^{2+} .

Main physical and mechanical properties of coatings, such as internal stresses and bonding strength to the substrate, can be demonstrated when a cathode with a sufficiently thick coating is bent. In the case of electrolytes with high pH values, copper coatings with satisfactory quality, that is, showing no fracture or peeling in bending, could not be obtained from ethylenediamine electrolytes of any composition or under any conditions producing glossy deposited coatings. In all cases, the gloss of deposits was accompanied by increase in internal stresses resulting in fracture of the coatings in bending (internal stresses occurring in deposition on a flexible cathode were compressive stresses). Another reason for lack of coating integrity in bending was weak bonding to the iron substrate due to passivation thereof in the presence of ethylenediamine.

We have found a condition under which high-quality matte deposits with a thickness of $20\text{--}30 \text{ }\mu\text{m}$ that are not fractured in cyclic bending can be formed on iron. The conversion of a free (in terms of complex ion formation) ethylenediamine into its salt that produces EnH^+ and EnH_2^{2+} cations when an acid is added up to a pH within a range of $7.3\text{--}7.8$ is such a condition. In

this case, the adsorption of ethylenediamine on iron that apparently causes poor adhesion of the coating and substrate is prevented.

The conversion of free ethylenediamine into ethylenediamine in chloride or sulfate solutions containing chloride ions at a very low concentration level (from 0.2 g/L) does not prevent poor bonding. The presence of chlorine ion facilitates the adsorption of ethylenediamine and its derivatives on iron. This is why such ion is the most harmful impurity in the baths of this type [4]. The harmful effect thereof can be neutralized by adding PbO at 0.1-0.2 g/L to the electrolyte. The suggested electrolyte composition contains $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.3-0.5 M, En 2-2.5 M, H_2SO_4 up to a pH value of 7.3-7.8, and PbO 0.1-0.2 g/L.

High cathode polarization in such electrolyte (600-800 mV at $D_k = 2 \text{ A/dm}^2$) ensures good dispersibility that is much better than in sulfate electrolytes for copper deposition and is only slightly worse than the dispersibility in cyanide solutions. The following differences between sulfate ethylenediamine electrolytes and chloride electrolytes are worth to be mentioned again: the anion nature ensures good adhesion in sulfate solutions and better dispersibility; in chloride solutions, the cathode polarization is several times lower than in sulfate solutions; and current yield values in both cases are the same.

The suggested electrolyte was tested by coating a number of machinery parts at an electrodeposition plant, and good results were obtained. Parts deposited with copper in this electrolyte were chromated and polished (on copper and chromium). These processes did not affect the bonding strength. Another advantage of the procedure is that the electrolyte is easy to prepare (aqueous solutions of components are mixed) and control (mainly, correction by pH).

Thus, the ethylenediamine electrolytes for copper deposition are superior to the conventional cyanide and acidic electrolytes. After thoroughly testing the electrolyte under industrial conditions, the industrial enterprises may consider purchasing ethylenediamine.

The possibility of zinc plating and cadmium deposition from ethylenediamine electrolytes containing 0.5 M $[\text{MeEn}_3]$ and 0.5-1.0 M En with various pH values was also studied. The results obtained demonstrated that although high-quality coatings can be obtained from these electrolytes under certain conditions, because such electrolytes have poor dispersivity (almost identical to that of simple acidic electrolytes), they can hardly be recommended for replacing the conventional acidic and cyanide electrolytes.

Electrode processes taking place in deposition of nickel and cobalt from ethylenediamine electrolytes have a large number of features that are of theoretical interest. However, the instability of solutions makes it practically impossible to perform long-term deposition of high-quality coatings. This instability is due to electrochemical behavior of ethylenediamine on nickel and cobalt anodes that catalytically accelerate the oxidation of ethylenediamine. At the same time, replacing soluble nickel and cobalt anodes with other anodes failed to resolve the problem. Because of a high degree of interdependence of cathodic and anodic processes, such a replacement causes structure deterioration in the cathodic deposits. The development of stable electrolytes seems to be promising because of a very high allowed current density (10-20 A/dm²) and high gloss of deposits obtained with freshly prepared electrolytes for nickel and cobalt deposition. This problem apparently can be solved by studying the specific features of anodic process.

Thus, additional research of ethylenediamine electrolytes for nickel and cobalt deposition is required.

Summarizing the obtained results relating to the possibility of using ethylenediamine for galvanic bath electrolytes, there is good reason to use ethylenediamine for copper deposition. Replacing sulfate copper electrolytes with ethylenediamine electrolytes makes it possible to obtain more uniform coatings and also enables the direct deposition of copper on iron. Further, ethylenediamine electrolytes for copper deposition can also replace cyanide electrolytes because the ethylenediamine electrolytes have lower toxicity and higher stability and ensure higher productivity than cyanide electrolytes.

On the other hand, ethylenediamine is still unsuitable for electrodeposition of other metals.

REFERENCES

1. Osetrova, N. V; Titov, P. S. NDVSh. Khimiya i Khim. Tekhnol., No. 4, 782, 1958.
2. Osetrova, N. V; Titov, P. S. NDVSh. Khimiya i Khim. Tekhnol., No. 1, 193, 1959.
3. Osetrova, N. V; Titov, P. S. NDVSh. Khimiya i Khim. Tekhnol., No. 3, 1959.
4. Osetrova, N. V; Titov, P. S. Izv. Visshikh Uchebnikh Zavedenii. Tsvetnaya Metallurgiya, No. 1, 1960..

5. Osetrova, Author's Certificate for "Electrolyte for Cyanide-free Deposition of Copper",
No. 621827, published on April 12, 1958.